Original Paper

Study on Improving Peroxide Value, Acetic acid-Isooctane Method Ⅲ

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Synopsis: AOCS, PV, Acetic Acid-Isooctane Method and JOCS PV Committee revised Method were proposed to be improved. The main points of improving are to make a homogeneous reaction mixture by revising each KI saturated solution to each 0.2 mL instead of 0.5 mL in AOCS method and 0.1 mL in JOCS one, and changing reaction period from just one minute in AOCS and one min. in JOCS to each 2 minutes in homogeneous solution. By revising these procedures, S.D. and C.V. of data were minimized, and the range of oxidizing reaction period is not serious but is permited to use 'about 2 min'.

1. Introduction

Peroxide value is an important indicator to check initial oxidizing step of fats and oils for edible purpose, and there are several measuring methods of it, for example AOCS or JOCS analytical method. Each method was revised from acetic acid-chloroform to acetic acid-isooctane as the solvent of reaction mixture by the standpoint of hygienics and pollution.

Though chloroform is polar organic solvent and reaction mixture of acetic acid-chloroform method forms homogeneous solution ordinarily except special case, isooctane is nonpolar solvent and forms homogeneous reaction mixture of potasium iodide saturated aqueous solution in merely narrow range without surfactant.

One of the authors discovered the homogeneous reaction mixtures area of triangle graph of three components (solvent: sample: KI saturated aqueous solution) (**Fig. 1**). It is very narrow range comparing with polar halogenated hydrocarbon mixture, but it can form a practically useful unilayer reaction mixture for analytical procedure without strong agitation.

The double layer reaction mixture with isooctane makes a trouble in obtaining an uniform result in KI oxidation and a surface layer of hydrophobic components interrupts correct titration in the iodometry, but the former trouble is minimised by the improved unilayer reaction mixture process, and by elongating oxidation reaction period from one minute to 2 minutes as shown in the following report.

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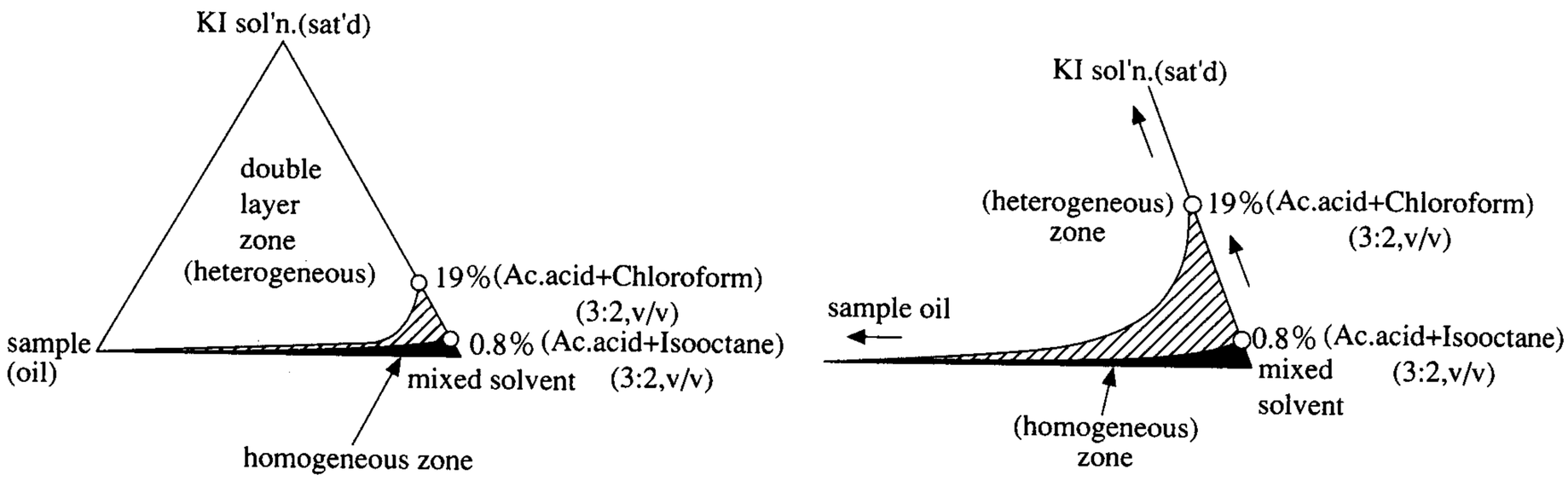


(a) Balance of 3 components[6]. (b) Enlarged Fig. of (a) right part[6].

Fig. 1 Triangle (phase diagram) of Reaction Mixture Components

2. Experiments

2.1 Preliminary PV measurement

The AOCS Recommended Practice Cd 80–90 (1990, revised 1991) was compared with official JOCS chloroform method empirically. **(Table 1)**

Table 1 Preliminary Measurement of PV

	AOCS isooct. method	JOCS chloroform method
Sample size, g	5.00	5.00
Solvent, mL	50.	30.
KI solution, mL	0.50	0.50
soybean oil A	av. 1.17	av. 0.917
no nitrogen replac.	av. 1.30	av. 1.21
soybean oil B	av. 5.64	av. 4.52
no nitrogen replac.	av. 5.31	av. 5.16

2.2 Sample size and KI solution volume

To sample size 5.0 g, KI solution 0.1 mL gave the result of 0.95 times PV to JOCS chloroform method, and about other cases more than 1.0 time were shown. The cause of this difference will be the length of reaction period because stoichiometrical quantity of KI is enough for oxidizing reaction in these cases.

Table 2 PV result ratio (chloroform, JOCS method=1.00)[6]

	—PV 30 range—				—PV 100 range—			
sample size, g	0.5	2.0	5.0	2.0	0.1	0.5	1.0	0.5
KI solution, mL	0.1	0.1	0.1	0.5	0.1	0.1	0.1	0.5
PV ratio to JOCS method	1.15	1.08	0.95	1.0	1.15	1.07	1.06	1.07

2.3 Phase separation phenomena of oxidizing reaction mixture

By revising merely KI solution volume in AOCS isooctane method, the phase separation of reaction mixture is not observed in the case of less than 0.3 mL. However, the more KI solution volume, the larger the reaction rate, and 0.2 or 0.3 mL KI solution is better than 0.1 mL one. **(Table 3)**

Table 3 phase separation

KI saturated aq. solution, mL	0.10	0.20	0.30	0.50
observed phase separation	none	none	none	observed
phase separation test numbers, times	0/6	0/6	0/6	6/6

2.4 Oxidation Period

Composition of Reaction Mixture	
sample size (rapeseed salad oil)	5.00 g
Mixed solvent (Ac. acid 3: Isooctane 2, vol/vol)	50 mL
KI sat. aq. solution	0.2 mL

The relation of reaction period and the observed PV was shown as follows in the case of above mentioned reaction at 20°C.

reaction period, min	1.0	2.0	3.0	4.0
observed PV, meq./kg	32.0	32.6	32.6	32.7

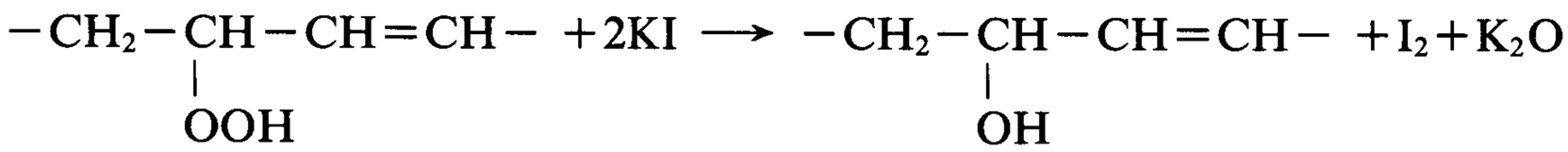
3. Results and Discussion

As the result of the above experiments, the preferable volume of KI saturated aqueous solution is 0.20 or 0.30 mL to make homogeneous reaction mixture in the AOCS style composition, however considering moisture rich samples the 0.2 mL is better than 0.3 mL.

Next, AOCS method took just one minute as the preferable reaction period, but in this case according to the concentration of one of the reactant KI solution is less than the AOCS case caused by 0.5 mL and reaction rate of hydroperoxide radical and KI. And 2.0 or 3.0 minutes may be adopted, but if N_2 gas replacement is not applied, the 2.0 minutes are better than 3.0 minutes. In this case, comparing just one minute with two minutes, the latter is easy for adjusting, and gives merely small error. When this reaction is generally discussed, following chemical equation will be appealed.

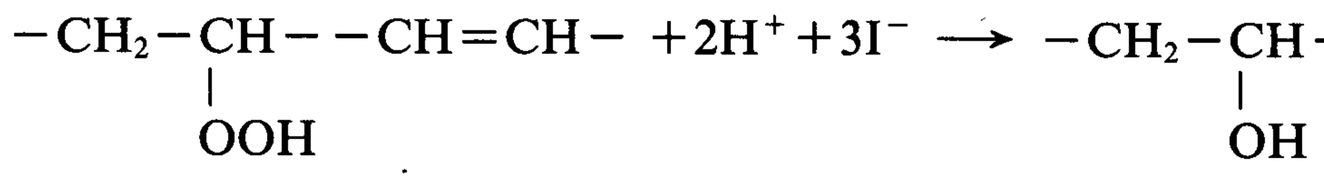
3.1 KI oxidation reaction by peroxiradical

3.1.1 Conventional equation (cf. Handbook of JOCS oil chemistry)[7)]

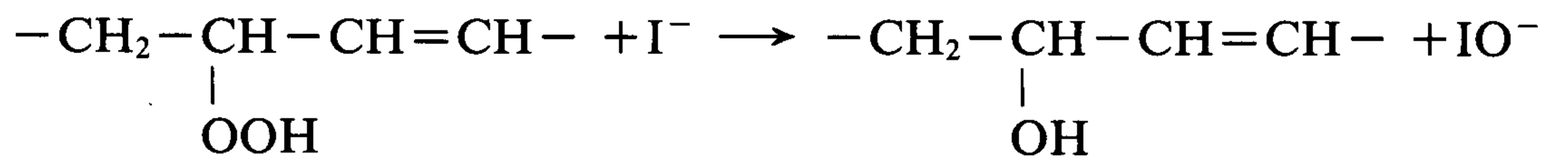


$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$$

3.1.2 Reaction under acetic acid acidic (analytical proposition),



The above equation will be separated as follows.



(1)

$$IO^- + H^+ \longrightarrow HIO \quad (2)$$

$$H^+ + I^- + HIO \longrightarrow {}^{H}{}_2O + I_2 \quad (3)$$

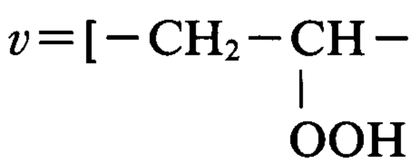
$$I^- + I_2 \longrightarrow I_3^- \quad (4)$$

As the result, KI stoichiometrical quantity may be 1.5 times that is I_3 equivalent weight to the traditional quantity corresponds to I_2. Though 2 mols of KI were considered to correspond to 1 mol of hydroperoxide, authors proposed that 3 mols of KI corresponded to 1 mol of hydroperoxide.

3.1.3 Stoichiometrical Discussion

In the former oxidation reaction, reaction rate controlling part may be the reaction of chemical equation (1).

In the equation (1) the reaction rate v of oxidation may be shown as follows.



Empirically, $\alpha + \beta = 2$

as the result, if $\alpha = 0$ or 1, $\beta = 2$ or 1

Isooctane is non polar organic solvent and I^-ion concentration in this solvent is less than that in chloroform solution, so the reaction rate of oxidation also may be less than in the traditional case. Some elongation of reaction period may occur, and 2 minutes as reaction period are reasonable.

Revising of quantity of KI solution from 0.5 mL to 0.2 mL, and elongation of reaction period from just one minute to two minutes needs each easier processing. The Standard Deviation and Coefficient of Variation of measured data in this method are smaller than that in the ordinary cases.

4. Conclusion

It may be some difficult to search unilayer reaction mixture, however in spite of its nar-

row range authors discovered the range empirically, as the results, easier checking reaction period does not need just one minute but (about) two minutes were adopted.

By these improvement, an easier processing can be adopted as a revised method.

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酢酸イソオクタン法過酸化物価測定法改良の研究（第3報）

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要旨　アメリカ油脂化学会による標記分析法の酸化反応液を単一の相に改良した前報に於ける反応を本報では化学反応論の立場から論じ，KIの量の減少で酸化反応速度が小となるため反応時間をAOCS法より長くして2 minが適当であることを見出した。

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